

10/539237

preferable, depending on the further use of the product stream, have such high selectivities of the  $\alpha$ -olefin.

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The olefinic feedstream may include ethylene and the  $(C_6 + C_8) : (C_4 + C_{10})$  ratio in the product stream may be more than 2.5:1.

The olefinic feedstream may include ethylene and the  $C_8 : C_6$  ratio in the product stream is more than 1.

The ethylene may be contacted with the catalyst system at a pressure of greater than 100 kPa (1 barg) and preferably greater than 1000 kPa (10 barg), more preferably greater than 3000 kPa (30 barg).

The heteroatomic ligand may be described by the following general formula  $(R)_nA-B-C(R)_m$  where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and R is independently selected from any homo or heterohydrocarbyl group of which at least one R group is substituted with a polar substituent and n and m is determined by the respective valence and oxidation state of A and C.

A and/or C may be a potential electron donor for coordination with the transition metal.

An electron donor or electron donating substituent is defined as that entity that donates electrons used in chemical, including dative covalent, bond formation.

The heteroatomic ligand may be described by the following general formula  $(R^1)(R^2)A-B-C(R^3)(R^4)$  where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from non-aromatic and aromatic, including heteroaromatic, groups of which at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is substituted with a polar substituent.

In some embodiments of the process aspect of the invention, up to four of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may have substituents on the atom adjacent to the atom bound to A or C.

the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, 1-hexene, 1-octene, ionic liquids and the like.

The process may be carried out at pressures from atmospheric to 50000 (500 barg). Ethylene pressures in the range of 1000-7000 kPa (10-70 barg) are preferred. Particularly preferred pressures range from 3000-5000 (30-50 barg).

The process may be carried out at temperatures from - 20 °C - 250 °C. Temperatures in the range of 15-130 °C are preferred. Particularly preferred temperatures range from 35-100°C.

In a preferred embodiment of the invention, the heteroatomic coordination complex and reaction conditions are selected such that the yield of 1-octene from ethylene is greater than 30 mass %, preferably greater than 35 mass %. In this regard yield refers to grams of 1-octene formed per 100g of total reaction product formed.

In addition to 1-octene, the process may also yield different quantities of 1-butene, 1-hexene, methylcyclopentane, methylene cyclopentane, propylcyclopentane, propylene cyclopentane and specific higher oligomers, depending on the nature of the heteroatomic ligand and the reaction conditions. A number of these products cannot be formed *via* conventional ethylene oligomerisation and trimerisation technologies in the yields observed in the present invention.

which the ice bath was removed. After stirring for a total of 14 hrs the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallisation in a 77 % yield.  $^{31}\text{P}$  {H} NMR: 47.4 ppm (broad singlet)

**Example 2: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl) $_2$ PN(methyl)P(4-methoxyphenyl) $_2$  and MAO**

A solution of 30.0 mg of (4-methoxyphenyl) $_2$ PN(methyl)P(4-methoxyphenyl) $_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 3000 kPa (30 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.2254 g of polyethylene. The GC analyses indicated that the reaction mixture contained 38.50g oligomers. The product distribution of this example is summarised in Table 1.

**Example 3: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (3-methoxyphenyl) $_2$ PN(methyl)P(3-methoxyphenyl) $_2$  and MAO**

A solution of 30.0 mg of (3-methoxyphenyl) $_2$ PN(methyl)P(3-methoxyphenyl) $_2$  (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO

(methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 3000 kPa (30 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.2269 g of polyethylene. The GC analyses indicated that the reaction mixture contained 9.71g oligomers. The product distribution of this example is summarised in Table 1.

**Example 4: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 36.1 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 3000 kPa (30 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.7105 g of polyethylene. The GC analyses indicated

that the reaction mixture contained 61.33g oligomers. The product distribution of this example is summarised in Table 1.

**Example 5: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 36.1 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 12 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 2.3010 g of polyethylene. The GC analyses indicated that the reaction mixture contained 73.53g oligomers. The product distribution of this example is summarised in Table 1.

**Example 6: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 16.4 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.03 mmol) in 10 ml of cyclohexane was added to a solution of 5.2 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml cyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of cyclohexane (80ml) and MAO (methylaluminoxane in toluene, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the

ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 11 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.9168 g of polyethylene. The GC analyses indicated that the reaction mixture contained 62.72g oligomers. The product distribution of this example is summarised in Table 1.

**Example 7: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 9.8 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.018 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 21 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.8280 g of polyethylene. The GC analyses indicated that the reaction mixture contained 69.17 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 8: Ethylene tetramerisation reaction using  $\text{Cr}(\text{III})$  2-ethylhexanoate,  $(4\text{-methoxyphenyl})_2\text{PN}(\text{isopropyl})\text{P}(4\text{-methoxyphenyl})_2$  and MAO**

A solution of 9.8 mg of  $(4\text{-methoxyphenyl})_2\text{PN}(\text{isopropyl})\text{P}(4\text{-methoxyphenyl})_2$  (0.018 mmol) in 10 ml of toluene was added to a solution of 5.6 mg  $\text{CrCl}_3 \cdot \text{THF}_3$  (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.0831 g of polyethylene. The GC analyses indicated that the reaction mixture contained 42.72 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 9: Ethylene tetramerisation reaction using  $\text{Cr}(\text{III})$  2-ethylhexanoate,  $(4\text{-methoxyphenyl})_2\text{PN}(\text{isopropyl})\text{P}(4\text{-methoxyphenyl})_2$  and MAO**

A solution of 9.8 mg of  $(4\text{-methoxyphenyl})_2\text{PN}(\text{isopropyl})\text{P}(4\text{-methoxyphenyl})_2$  (0.018 mmol) in 10 ml of toluene was added to a solution of 10.2 mg  $\text{Cr}(\text{III})$  2-ethylhexanoate (70% in mineral oil, 0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after

30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.52 g of polyethylene. The GC analyses indicated that the reaction mixture contained 61.27 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 10: Ethylene tetramerisation reaction using Cr (III) octanoate , (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 9.8 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.018 mmol) in 10 ml of toluene was added to a solution of 10.3 mg Cr (III) octanoate (70% in toluene, 0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 40 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.3773 g of polyethylene. The GC analyses indicated that the reaction mixture contained 18.91 g oligomers. The product distribution of this example is summarised in Table 1.



**Example 11: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 6.6 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.012 mmol) in 10 ml of toluene was added to a solution of 3.5 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 3.0 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.3958 g of polyethylene. The GC analyses indicated that the reaction mixture contained 54.52 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 12: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 9.8 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.018 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane in toluene, 2.25 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by

discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.5010 g of polyethylene. The GC analyses indicated that the reaction mixture contained 70.87 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 13: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MMAO-3A**

A solution of 16.4 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.03 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MMAO-3A (modified methylaluminoxane in heptanes, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 22 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.76 g of polyethylene. The GC analyses indicated that the reaction mixture contained 50.42g oligomers. The product distribution of this example is summarised in Table 1.

**Example 14: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and EAO/TMA**

A solution of 36.1 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml), EAO (ethylaluminumoxane in toluene, 33 mmol) and TMA (trimethylaluminium, 8.25mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.189 g of polyethylene. The GC analyses indicated that the reaction mixture contained 40.97g oligomers. The product distribution of this example is summarised in Table 1.

**Example 15: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> and MAO in the presence of H<sub>2</sub>**

A solution of 16.4 mg of (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub> (0.03 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminumoxane in toluene, 4.5 mmol) at 40°C. The pressure reactor was first charged with hydrogen to a pressure of approximately 250 kPa (2.5 barg) and subsequently with ethylene to 4500 kPa (45 barg) after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100

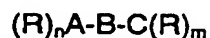
RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.2060 g of polyethylene. The GC analyses indicated that the reaction mixture contained 81.51 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 16: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (phenyl)<sub>2</sub>PN(isopropyl)P(2-methoxyphenyl)<sub>2</sub> and MAO**

A solution of 32.2 mg of (phenyl)<sub>2</sub>PN(isopropyl)P(2-methoxyphenyl)<sub>2</sub> (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane in toluene, 4.5 mmol) at 40°C. The pressure reactor was first charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 4500 kPa (45 barg). Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 6.82 g of polyethylene. The GC analyses indicated that the reaction mixture contained 38.33 g oligomers. The product distribution of this example is summarised in Table 1.

1. A process for the oligomerisation of olefins which includes the step of contacting an olefinic feedstream with a catalyst system which includes the combination of:

- a transition metal compound; and
- a heteroatomic ligand described by the following general formula



where

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different and each R is independently selected from a homo hydrocarbonyl group and a heterohydrocarbonyl group, and at least one R is substituted with a polar substituent; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group;

at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ , if aromatic is substituted with a polar substituent on a 2<sup>nd</sup> or further atom from the atom bound to A or C and provided that any polar substituents on  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ , if they are aromatic, are not on the atom adjacent to the atom bound to A or C.

2. The process as claimed in claim 1 wherein the heteroatomic ligand is described by the following general formula  $(R^1)(R^2)A-B-C(R^3)(R^4)$  where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth, and nitrogen; B is a linking group between A and C; and each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group.
3. The process as claimed in claim 2, wherein up to four of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  have substituents on the atom adjacent to the atom bound to A or C.
4. The process as claimed in claim 2 which is a tetramerisation process and wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is aromatic, including heteroaromatic, but not all of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are substituted by a substituent on an atom adjacent to the atom bound to A or C.
5. The process as claimed in claim 4, wherein not more than two of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  have substituents on the atom adjacent to the atom bound to A or C.
6. The process as claimed in any one of claims 2 to 5, wherein each polar substituent on one or more of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is electron donating.
7. The process as claimed in either one of claims 4 or 5 wherein the feedstream includes an  $\alpha$ -olefin and the product stream includes at least 30% of a tetramerised  $\alpha$ -olefin monomer.
8. The process as claimed in claim 7 wherein the olefinic feedstream includes ethylene and the product stream includes at least 30% 1-octene.
9. The process as claimed in any one of claims 1 to 8 wherein the olefinic feedstream includes ethylene and wherein the  $(C_6 + C_8) : (C_4 + C_{10})$  ratio in the product stream is more than 2.5:1.
10. The process as claimed in either one of claims 1 or 4, wherein the olefinic feedstream includes ethylene and wherein the  $C_8 : C_6$  ratio in the product stream is more than 1.

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11. The process as claimed in any one of claims 1 to 10 where the pressure is greater than 100 kPa (1 barg).
12. The process as claimed in any one of claims 8 to 10 wherein ethylene is contacted with the catalyst system at a pressure of more than 1000 kPa (10 barg).
13. The process as claimed in any one of claims 1 to 12 wherein A and/or C are a potential electron donor for coordination with the transition metal.
14. The process as claimed in any one of claims 1 to 13 wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, a substituted hydrocarbyl, a hetero hydrocarbyl or a substituted hetero hydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine,  $-B(R^5)-$ ,  $-Si(R^5)_2-$ ,  $-P(R^5)-$  and  $-N(R^5)-$  where  $R^5$  is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
15. The process as claimed in claim 14 wherein B is a single atom linking spacer.
16. The process as claimed in claim 14 wherein B is  $-N(R^5)-$ , wherein  $R^5$  is selected from the groups consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.
17. The process as claimed in any one of claims 1 to 16, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
18. The process as claimed in any one of claims 1 to 16, wherein A and C is independently phosphorous or phosphorous oxidised by S or Se or N or O.
19. The process as claimed in claim 2 wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from the group consisting of benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl,

thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.

20. The process as claimed in claim 1 or claim 2 wherein the ligand is selected from the group consisting of (3-methoxyphenyl)<sub>2</sub>PN(methyl)P(3-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(methyl)P(4-methoxyphenyl)<sub>2</sub>, (3-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(3-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(2-ethylhexyl)P(4-methoxyphenyl)<sub>2</sub>, (3-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)<sub>2</sub> and (4-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)<sub>2</sub>, (3-methoxyphenyl)(phenyl)PN(methyl)P(3-methoxyphenyl)(phenyl), (4-methoxyphenyl)(phenyl)PN(methyl)P(4-methoxyphenyl)(phenyl), (3-methoxyphenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub> and (4-methoxyphenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(1-cyclohexylethyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(2-methylcyclohexyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(decyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(pentyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(benzyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(phenyl)P(4-methoxyphenyl)<sub>2</sub>, (4-fluorophenyl)<sub>2</sub>PN(methyl)P(4-fluorophenyl)<sub>2</sub>, (2-fluorophenyl)<sub>2</sub>PN(methyl)P(2-fluorophenyl)<sub>2</sub>, (4-dimethylamino-phenyl)<sub>2</sub>PN(methyl)P(4-dimethylamino-phenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(allyl)P(4-methoxyphenyl)<sub>2</sub>, (4-(4-methoxyphenyl)-phenyl)<sub>2</sub>PN(isopropyl)P(4-(4-methoxyphenyl)-phenyl)<sub>2</sub> and (4-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)<sub>2</sub>.

21. The process as claimed in any one of claims 1 to 20 wherein the catalyst system is prepared by combining in any order the heteroatomic ligand with the transition metal compound and an activator.

22. The process as claimed in claim 21, which includes the step of adding a pre-formed coordination complex, prepared using the heteroatomic ligand and the transition metal compound, to a reaction mixture containing the activator.

23. The process as claimed in claim 21, which includes the step of generating a heteroatomic coordination complex *in situ* from the transition metal compound and a heteroatomic ligand.

24. The process as claimed in any one of the claims 1 to 23, wherein the transition metal in the transition metal compound is selected from the group



consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.

25. The process as claimed in claim 24, wherein the transition metal is chromium.

26. The process as claimed in any one of claims 1 to 25, wherein the transition metal compound is selected from the group consisting of an inorganic salt, an organic salt, a co-ordination complex and an organometallic complex.

27. The process as claimed in claim 26 wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.

28. The process as claimed in claim 27, wherein the transition metal compound is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

29. The process as claimed in any one of claims 1 to 28, wherein the transition metal from the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.

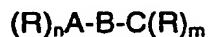
30. The process as claimed in any one of claims 21 to 23 wherein the catalyst system includes an activator selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, such as methyl lithium and methylmagnesium bromide, an inorganic acid and salt, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

31. The process as claimed in claim 30, wherein the activator is an alkylaluminumoxane.

32. The process as claimed in claim 31, wherein the transition metal compound and the aluminumoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.

33. A tetramerisation catalyst system which includes the combination of:

- a transition metal compound; and
- a heteroatomic ligand described by the following general formula



where

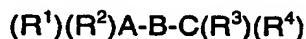
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different and each R is independently selected from a homo hydrocarbyl group and a heterohydrocarbyl group, and at least one R is substituted with a polar substituent; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group;

at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ , if aromatic is substituted with a polar substituent on a 2<sup>nd</sup> or further atom from the atom bound to A or C and

provided that any polar substituents on  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ , if they are aromatic, are not on the atom adjacent to the atom bound to A or C.

34. The catalyst system as claimed in claim 33 wherein the heteroatomic ligand is described by the following general formula  $(R^1)(R^2)A-B-C(R^3)(R^4)$  where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony,

bismuth, and nitrogen; B is a linking group between A and C; and each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group.

35. The catalyst system as claimed in claim 34 wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is aromatic, including heteroaromatic, but not all of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are substituted by a substituent on an atom adjacent to the atom bound to A or C.

36. The catalyst system as claimed in claim 35, wherein not more than two of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  have substituents on the atom adjacent to the atom bound to A or C.

37. The catalyst system as claimed in any one of claims 34 to 36, wherein each polar substituent on one or more of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is electron donating.

38. The catalyst system as claimed in any one of claims 33 to 37, wherein A and/or C are a potential electron donor for coordination with the transition metal.

39. The catalyst system as claimed in any one of claims 33 to 38, wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, a substituted hydrocarbyl, a hetero hydrocarbyl and a substituted hetero hydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine,  $-B(R^5)-$ ,  $-Si(R^5)_2-$ ,  $-P(R^5)-$  and  $-N(R^5)-$  where  $R^5$  is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.

40. The catalyst system as claimed in claim 39, wherein B is a single atom linking spacer.

41. The catalyst system as claimed in claim 39, wherein B is selected to be  $-N(R^5)-$ , wherein  $R^5$  is selected from the groups consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxy, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.

42. The catalyst system as claimed in any one of claims 33 to 41, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.

43. The catalyst system as claimed in any one of claims 33 to 41, wherein A and C is independently phosphorus or phosphorus oxidised by S or Se or N or O.

44. The catalyst system as claimed in any one of claims 1 to 43 wherein the ligand is selected from the group consisting of (3-methoxyphenyl)<sub>2</sub>PN(methyl)P(3-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(methyl)P(4-methoxyphenyl)<sub>2</sub>, (3-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(3-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(isopropyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(2-ethylhexyl)P(4-methoxyphenyl)<sub>2</sub>, (3-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)<sub>2</sub> and (4-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)<sub>2</sub>, (3-methoxyphenyl)(phenyl)PN(methyl)P(3-methoxyphenyl)(phenyl), (4-methoxyphenyl)(phenyl)PN(methyl)P(4-methoxyphenyl)(phenyl), (3-methoxyphenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub> and (4-methoxyphenyl)<sub>2</sub>PN(methyl)P(phenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(1-cyclohexylethyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(2-methylcyclohexyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(decyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(pentyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(benzyl)P(4-methoxyphenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(phenyl)P(4-methoxyphenyl)<sub>2</sub>, (4-fluorophenyl)<sub>2</sub>PN(methyl)P(4-fluorophenyl)<sub>2</sub>, (2-fluorophenyl)<sub>2</sub>PN(methyl)P(2-fluorophenyl)<sub>2</sub>, (4-dimethylamino-phenyl)<sub>2</sub>PN(methyl)P(4-dimethylamino-phenyl)<sub>2</sub>, (4-methoxyphenyl)<sub>2</sub>PN(allyl)P(4-methoxyphenyl)<sub>2</sub>, (4-(4-methoxyphenyl)-phenyl)<sub>2</sub>PN(isopropyl)P(4-(4-methoxyphenyl)-phenyl)<sub>2</sub> and (4-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)<sub>2</sub>.

45. The catalyst system as claimed any one of the claims 33 to 44, wherein the transition metal in the transition metal compound is selected from the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.

46. The catalyst system as claimed in claim 45, wherein the transition metal is chromium.

47. The catalyst system as claimed in any one of claims 33 to 46, wherein the transition metal compound is selected from the group consisting of an inorganic salt, an organic salt, a co-ordination complex and an organometallic complex.

48. The catalyst system as claimed in claim 47, wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.

49. The catalyst system as claimed in of claim 48, wherein the transition metal is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

50. The catalyst system as claimed in any one of claims 33 to 49, wherein the transition metal from the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.

51. The catalyst system as claimed in any one of claims 33 to 50, which includes an activator.

52. The catalyst system as claimed in claim 51, wherein the activator is selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, such as methyl lithium and methylmagnesium bromide, an inorganic acid and salt, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

53. The catalyst system as claimed in claim 52, wherein the activator is an alkylaluminumoxane.

54. The catalyst system as claimed in claim 53, wherein the alkylaluminumoxane is selected from the group consisting of methylaluminumoxane (MAO), ethylaluminumoxane (EAO) modified alkylaluminumoxanes (MMAO), and mixtures thereof.

55. The catalyst system as claimed in claim 53 or claim 54, wherein the transition metal and the aluminumoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.

56. Use of a catalyst system as claimed in any one of claims 33 to 55 for the tetramerisation of olefins.

57. Use of a catalyst system as claimed in any one of claims 33 to 55 for the tetramerisation of ethylene.

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